

LDF CALCULATIONS OF POINT DEFECTS IN GRAPHITES AND FULLERENES

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Abstract

Using a spin density functional code (AIMPRO) we have examined the properties of interstitials and adatoms on graphite (modelled as one, two or three layers of a polyaromatic hydrocarbon $C_{62}H_{20}$) and on a number of fullerenes. We report the structure, bonding and energetics of these defects and give an account of their mobilities. Their formation energies are high and properties are spin-dependent, making parametrised potentials and simplified tight binding schemes inappropriate.

For the adatom we find a very mobile triplet state in which the carbon atom is partially ionically bound and a singlet state in which the atom is located above a C–C bond center. For the interstitial we find a structure analogous to spiro-pentane in which the interstitial forms

two almost equilateral triangular rings with pairs of carbon atoms in adjacent layers.

A model presented earlier for the structure of quasi-spherical carbon onions requires that the autocatalysis mechanism for Stone-Wales transformations be catalysed by carbon adatoms. We therefore present calculations of the activation energies for these catalysed processes as a function of substrate (graphite/fullerene) curvature to extend the earlier work on C_{60} .

INTRODUCTION

Interstitials play a crucial role in the structural deformation of graphite [1]. Both high energy irradiation and grinding generate interstitial:vacancy pairs in graphite. At high temperatures, vacancies aggregate and reconstruct, while interstitials aggregate between the basal planes and form new layers. This process, known as *plating out*, leads to an anisotropic change in the dimensions of graphitic grains [2] and more recently has been proposed as a model for the formation of carbon onions [3]. At low temperatures the annealing process is incomplete and the defect subsystem results in the storage of substantial amounts of energy.

Various experimental techniques have been used to study point defects: (concentration of quenched-in vacancies, analysis of stored energy, specific heat etc.) and formation energies of 7 eV have been inferred for both the vacancy and the self-interstitial [2] with an uncertainty of 0.5 eV for the vacancy and 1.5 eV for the interstitial [4].

No first principles calculations have been reported to date on interlayer interstitial defects, with the exception of a brief mention of the formation energy of the adatom (3.3 eV) given in a work dominated by the application of Tersoff's potential [5]. Earlier work includes application of an interatomic potential in which the energy of an atom depends on the Wigner-Seitz or 'proximity' cell around the atom [6] and the application of a tight-binding technique [7]. The first concluded that the interlayer interstitial lay bonded between host atoms above one another in different planes (the 'Wallace structure' [8]) and the second that most sites are equivalent in energy (including the structure in which the interstitial lay between an atom in one layer and the centre of a hexagon in the other layer [4]) apart from the Wallace interstitial which lay higher in energy. Interestingly, the proximity cell work indicated that interstitials in neighbouring layers could bond to each other and could in fact form strings in the *c* direction [9].

Here we detail the geometrical and electronic structure of the adatom, the interstitial and its propensity to form strings. We also investigate how the adatom catalyses changes in ring statistics, in the same fashion as the autocatalysis mechanism for C_{60} growth [10].

I. METHOD

The calculations presented here are first principle calculations (i.e. require only the atomic numbers for calculation and involve no experimental parametrisation). The program used, AIMPRO [11], invokes Density Functional Theory within the Local Spin Density Approximation for exchange and correlation [12]. Norm-conserving pseudopotentials of ref. [13] were used, since these remove the need to include core electrons in the calculation. Since the method is real space and therefore finite, the graphite sheet has to be hydrogen terminated at the edge. This leads to a polyaromatic hydrocarbon sheet, $C_{62}H_{20}$. Where we examined the nature of interstitials between graphitic sheets, two of these polyaromatic sheets were used in the same calculation, offset to simulate AB stacking.

A real-space basis is used, with 16 Gaussians per graphite carbon atom (4 each of s -, p_x -, p_y - and p_z - symmetry) and 12 per hydrogen atom to model the molecular wavefunctions; 4 s -type Gaussians were used for the valence charge density per carbon or hydrogen. This method is extremely efficient for systems of up to 1000 atoms, and has proved itself able to accurately model similar carbon-hydrogen based systems such as fullerenes and diamond surfaces [10,14]. The self-consistent energy E and the force on each atom were calculated and the atoms moved by a conjugate gradient algorithm until equilibrium was attained.

Taking differences in energy between polyaromatics which differ only in the number of carbon atoms [15] we obtain a cohesive energy for graphene of between 7.2 eV and 7.6 eV, depending on basis set and size of graphene molecule. Furthermore, we find C-C intra-planar bonds with a mean length of 1.42 Å, interlayer separation of 2.95 Å and energy of 52 meV/atom in AB stacking. The experimental values are 7.34 eV for the cohesive energy of graphene [16], and 3.35 Å separation between the graphitic sheets. The cluster method thus slightly overbinds the layers and the interlayer distance is contracted. However, Charlier *et al.* [17–19] have shown that a similar, but supercell-based, DFT method does give a correct description of the inter-planar interaction in graphite with an energy 25 meV/atom.

THE CARBON ADATOM

Recently, Nordlund and coworkers [5] calculated an adatom formation energy of 5.8 eV with the Tersoff potential, and of 3.3 eV with an LDA formalism, placing the extra atom above a C-C bond centre. They found that the lowest energy structure is one where the carbon atom adds to a C-C host bond to form an equilateral carbon triangle perpendicular to the plane of the sheet. The high value of adatom binding appears difficult to reconcile with the high formation energy of the graphite interstitial, which almost equals the cohesive energy and corresponds to very weak effective binding.

We relaxed a singlet carbon adatom on graphite in a variety of different configurations and found the lowest energy structure was a triangular carbon structure with formation energy 1.2 eV. (The absolute value of this binding energy must be treated with caution since the cohesive energies of graphite and diamond in LDA can be up to 1 eV too large [16]). The C-C bond lengths are 1.54 Å, with bond angles close to 60°. In order to incorporate this extra atom into the bond, the original graphite C-C bond is dilated by 7 % to 1.55 Å, but does not open in the ground state and the two graphitic C atoms are pushed backwards and slightly out of plane. (Opening can occur in clusters smaller than C₆₂H₂₀).

When the adatom electron occupation was modified to the triplet spin state, $S = 1$, the adatom spontaneously moved out of the above-bond-centre to a position 2.1 Å above the graphite plane, before drifting away from the bond centre site to lie directly above a lattice carbon atom. This structure is almost degenerate in energy with the singlet structure (being 0.15 eV lower, but LSDA is known to favour high spin states). During its path, from above-bond-centre to above-atom, the energy varied by less than 0.1 eV, indicating that the triplet adatom is highly mobile.

Early LDA calculations on in-plane defects in graphite [20] revealed that penetration of the plane through void regions was prohibitively energetic (19.5 eV). Therefore we examine here interstitialcy-like motion through an {0001} split-interstitial and find a metastable {0001} split interstitial with energy of 0.5 eV above ground state. We have not as yet located the strict saddle point for this motion, but find one of the intermediate states at 0.7 eV above ground state (*c.f.* 2.3 eV found by a tight-binding method [7]).

If we take the adatom as a model for interstitial behaviour then the similarity between diffusion parallel to the plane (*ca.* 0.1 eV as a triplet) and perpendicular to the plane (*ca.* 0.7 eV through the split interstitial) could explain the almost isotropic behaviour for the activation energy for boron diffusion [2] (which includes the standard energy of formation for the adatom of 6.1 eV).

Taking the adatom model further we can examine two different ways in which interstitials combine: forming strings along the *c* direction and aggregating in the *a* direction. Consider two neighbouring host atoms in the graphene sheet. Apart from their mutual bond, they each have two further bonds. Placing an adatom on one such bond of each such host atom (on opposite sites of the sheet) yields a diadatom configuration 2.3 eV lower in energy than the isolated adatoms. This energy saving must be related to what can be expected when interstitials form a *c* string. Aggregation within the basal plane occurs when two adatoms bond to each other as they are sited above the centres of two parallel host C-C bonds in the same hexagon. The energy of this diadatom, comprising two adjacent pentagons, is 5.6 eV, *i.e.* 6.4 eV below the isolated adatoms.

INTER-PLANAR INTERSTITIAL

While we have studied a variety of interplanar locations as starting points, singlet occupation always led to a basal plane shift of half the intraplanar interatomic distance between the planes and the formation of a structure in which the interstitial took part in two corner-sharing, almost equilateral, triangular rings. The interstitial was thus bound to two mutually bonded host carbon atoms in each plane, the planes of the resulting triangles making an angle of 60° . This structure was obtained in a cluster with free boundary conditions, which may well be a better representation of graphite in which basal dislocations freely form and move. The large basal shift presumably explains the strong coupling between the point defect interstitial and the rather diffuse core of a basal dislocation.

The five core atoms resemble the spiro-pentane C_5H_8 molecule, hence we name the structure the *spiro-interstitial*. Spiropentane is a rather stable molecule (up to $360^\circ C$ [21]) with a dihedral angle of 90° and heat of formation of 185 kJmol^{-1} [22] (AIMPRO heat of formation 179 kJmol^{-1}). AIMPRO gave bond lengths 1.47 \AA and base angles of 63° in excellent agreement with an X-ray structure analysis [23], which found 1.48 \AA and 63° , respectively.

In order to understand the high formation energy of the interstitial and where it comes from, we calculated heats of reaction for a carbon atom reacting with two ethene molecules to yield spiro-pentane and with two C_{60} molecules to yield an equivalent C_{121} spiro structure. Both were in the region of 6-7 eV (6.3 eV, respectively, compared with -1.2 eV for the spiro-interstitial, much reduced by disruption of in-plane π bonds and deviation from a dihedral angle of 90° . Whereas the adatom had a binding energy of 1.2 eV by taking part in one bonding triangle, the interstitial is not able to increase this binding in two triangles presumably because of the unfavourable dihedral bond angle.

It is interesting to note that all atoms in the spiro-interstitial are either 3- or 4-fold coordinated and that the defect is spin-free.

While the adatom formed a triplet state upon an enforced change in electron occupation, we have been unable to make this happen in the triplet. A first attempt starting from the spiro-structure resulted in the two unpaired spins going into almost degenerate graphite host orbitals from the two sheets. A second attempt, starting from a structure optimised for an intercalated Li atom which was then converted to a triplet carbon, proved to be 3 eV higher than the singlet state and resulted in the ejection of the interstitial through one of the graphite planes via an interstitialcy mechanism, giving a triplet adatom. Since the triplet adatom requires greater than 2 \AA separation from the graphene sheet, the barrier to expansion of the interlayer separation beyond 4 \AA might cause its instability.

STONE-WALES TRANSFORMATIONS

In the controversy of “fullerene” road versus “pentagon” road of fullerene growth, Stone-Wales transformations play a crucial role. Accretion of carbon to small fullerenes will most likely form intermediate fullerenes in which pentagons neighbour one another. SW transformations can then rearrange the ring structure to produce isomers that conform to the Isolated Pentagon Rule.

Furthermore, it has been suggested that changes in ring statistics of carbon shells brings about the quasi-spherical appearance of carbon onions formed under irradiation [24]. In onion formation [3] sputtering from the carbon shells by radiation leads to reduced shell sizes and hence compression (eventually forming diamond in the inner region [25]). Since radiation damage (*i.e.* sputtering) leads to formation of interstitial carbon atoms, then they might be available to catalyse the SW transformations necessary to approach sphericity in the same way as they have been shown to do in an isolated C_{60} molecule [10]. However, there are distinct differences between the behaviour of C_{60} and the series of higher (larger radius of curvature) fullerenes that make the onion (for which the limiting case is a graphene sheet, *i.e.* infinite curvature). Here we calculate the SW transformation energetics for a 51 atom patch of C_{240} (post hydrogenated to give $C_{51}H_{15}$) and for a 62 atom patch of graphite (post hydrogenated to give $(C_{62}H_{20})$). Not all SW transformations are equivalent in C_{240} —we studied two of them near the apical pentagon and report the lowest energy case.

Table 1 shows that SW transformations are more progressively more difficult in the larger fullerenes and in graphite. SW transformations disrupt aromaticity and can be more easily accommodated out of plane. Thus the increasing trend in activation energy probably comes from the increasing aromaticity and increasing radius of curvature in the progression C_{60} , C_{240} , graphite. In spite of this trend, the catalytic effect still applies and the activation energy to remove the SW product (in the limited cases chosen here) is actually reduced with increasing fullerene size (to 2.5 eV in the case of graphite).

Energetics of Stone-Wales transformations (in eV)

Substrate	uncatalysed activation energy	product energy	catalysed activation energy	net reduction in activation energy	
C_{60}	6.2	1.5	4.0	2.2	†
C_{240} ($C_{51}H_{15}$)†	7.6	2.0	4.8	2.8	
graphite ($C_{62}H_{20}$)	8.8	3.4	6.1	2.7	
lowest of two alternatives					

CONCLUSIONS

Point interstitial defects within graphite are characterised by large bonding rearrangements leading to extra bonds which have lengths corresponding to reasonably strong single bonds. Nevertheless the net effect of all bonding is weak because of the cost of disrupting the delocalised π bonding within the sheets. Similarly, movement of interstitials through graphene sheets can occur relatively easily via an interstitialcy mechanism (rather than through void regions) with large bonding rearrangements, because of the low energy of formation of $\{0001\}$ split interstitials.

Finally, the autocatalysis mechanism for carbon growth, which had been shown to apply to C_{60} as a special case, has been shown to apply more generally to fullerenes and graphite.

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